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Chemical Vapor Deposition

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Photo-oxidation of polymers synthesized by plasma and initiated chemical vapor deposition

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ABSTRACT

Plasma polymers are often limited by their susceptibility to spontaneous and photo-oxidation. We show that the unusual photoluminescence (PL) behavior of a plasma polymer of *trans*-2-butene is correlated with its photoluminescence strength. These photo-processes occur under blue light illumination (λ=405 nm), distinguishing them from traditional ultraviolet degradation of polymers. These photo-active defects are likely formed during the plasma deposition process and we show that a polymer synthesized using initiated CVD, non-plasma method, has 1000× lower PL signal and enhanced photo-stability. Non-plasma methods such as iCVD may therefore be a route to overcoming material aging issues that limit the adoption of plasma polymers.

Keywords: plasma polymers, photo-oxidation, photoluminescence, initiated CVD, stability

Introduction

Plasma polymerization, one of the major synthetic technologies for chemical vapor deposition (CVD) of polymers, is based on the fragmentation of an organic gas in a plasma discharge. These reactive fragments then form a polymer-like material on a solid substrate. Plasma polymerization can produce highly cross-linked polymer-like films, giving them desirable mechanical and thermal stability properties. However, the fragmentation during polymerization can also lead to the incorporation of chemical and electronic defects in the polymer.[1, 2] These defects – particularly carbon-centered free radicals – are reactive with water and molecular oxygen, causing plasma polymers to age when they are exposed to the ambient environment. Thus, the mechanical and thermal stability of plasma polymers is often overshadowed by a lack of chemical stability, one of the major hurdles in the wide-scale adoption of CVD polymers.[3]

We use hydrocarbon CVD polymers – in particular, a plasma polymer of *trans*-2-butene – as ablators in high energy density (HED) science applications such as inertial confinement fusion research.[4] This work was motivated by the need to find routes toward chemically stable hydrocarbon CVD polymers for use as HED ablators, which for decades have been synthesized by plasma polymerization of *trans*-2-butene.[5] HED ablators have demanding requirements on both overall and variations in chemical composition, making them very sensitive to the effects of aging in ambient conditions.[6] They are therefore an interesting test case for the development of strategies to enhance the chemical stability of CVD polymers, which may ultimately find wider application in a variety of packaging and protection applications.

In this work, we are concerned with the photo-oxidative stability of hydrocarbon CVD polymers under blue light (λ = 405 nm) illumination. Photo-oxidation of polymers under ultraviolet (UV) illumination is a widely studied phenomenon and is based on UV-induced bond

breakage. We wished to study processes unique to plasma polymers and chose a longer wavelength that would not simply reproduce classical UV polymer photo-oxidation. Photo-oxidative stability is important not only for materials in direct contact with light, but also because of the ubiquitous use of light-curing adhesives (increasingly utilizing blue light[7]) and visible light metrology techniques.

The stability of plasma polymers has long been studied in the context of spontaneous oxidation due to contact with ambient air and water. Three main strategies can be found in the literature to enhance the chemical stability of plasma polymers: 1) copolymerization, 2) chemical passivation, and 3) thermal annealing.[1, 8, 9] Of the three, thermal annealing is the most convenient and has the least impact on the polymer chemistry since it does not require the incorporation of new precursor materials. Plasma polymers that are thermally annealed generally show much greater chemical stability under ambient conditions.[9, 10]

Despite the attention given to spontaneous oxidation of plasma polymers, there are few reports on the photostability of plasma polymers. In this work, we show that thermal annealing of a *trans*-2-butene plasma polymer makes it less photostable, not more, when illuminated by blue light in the presence of oxygen. Use of blue light, rather than UV light, distinguishes the phenomena we observe from classical UV-induced polymer photo-oxidation. We connect the photo-oxidation of the plasma polymer to unusually strong and disordered photoluminescence (PL) behavior characteristic of plasma polymers. This PL behavior is consistent with previous research[1, 11-13] and is characterized by high intensities and overall decay lifetimes on the order of nanoseconds that do not behave as simple exponentials.

We show that the PL has the hallmarks of a phenomenon known as quasi-continuum PL (QCPL), which is caused by the absorption and emission of light in a material containing a high

density of defects.[14] The strength of this QCPL is correlated to the rate of photo-oxidation of the plasma polymer under blue light illumination. The strength of this PL increases, rather than decreases, after thermal annealing. Correspondingly, the rate of photo-oxidation is faster in the thermally annealed plasma polymer than in the as-deposited plasma polymer. Free radicals formed during plasma polymerization, typically implicated in the aging and degradation of plasma polymers, are not directly responsible for photo-oxidation.

As an alternative to plasma polymerization, we synthesized polydivinylbenzene (PDVB) using a plasma-free process known as initiated CVD (iCVD).[15, 16] The iCVD polymer retains the structural features of its divinylbenzene (DVB) monomer, consistent with previous reports. The polymer synthesized with this plasma-free process exhibits less PL, and correspondingly greater photo-oxidative stability, suggesting that the defects causing the photoactivity of plasma polymers may originate from the plasma fragmentation of the precursor gas.

Results and discussion

Fourier transform infrared (FTIR) spectra of the as-deposited and annealed plasma polymers are shown in Figure 1. As the plasma polymer is deposited from a hydrocarbon precursor, C-C and C-H stretches dominate the spectra. Most prominent is the large peak between 2800 and 3000 cm^{-1}, which corresponds to aliphatic C-H stretches. The strong stretches at 1456 cm^{-1} and 1376 cm^{-1} can be assigned to C-H bending modes. These features are relatively insensitive to annealing at either 200 $^{\circ}$C or 300 $^{\circ}$C.
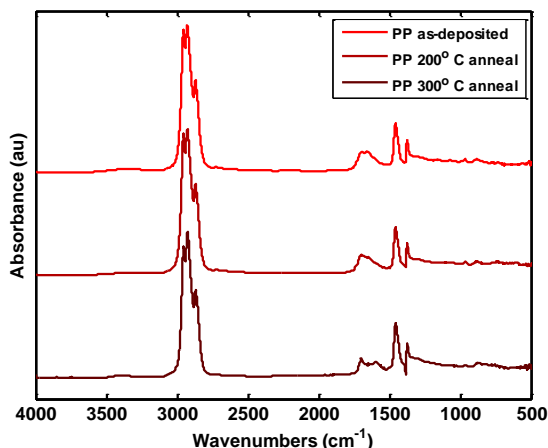
Figure 1. FTIR spectra for plasma polymer (PP) as deposited, after 200 ^{o}C anneal, and after 300°C anneal.

However, stretches associated with oxygen can be found in these spectra and are affected by annealing. The most obvious of these is a carbonyl stretch at 1710 cm^{-1}. More subtle, although visible upon close inspection (see, for example, the bottom spectrum in Figure 1), is a broad peak in the 3100-3600 cm^{-1} range. As these samples were deposited in oxygen-free plasma from hydrocarbon precursors and annealed under nitrogen, the oxygen in the plasma polymer can be considered a post-deposition contaminant. Spontaneous oxidation of plasma polymers in ambient air is a well-known phenomenon, and the as-deposited sample likely underwent reaction with molecular oxygen in the short time (minutes) between removal from storage and placement into the nitrogen-purged FTIR sample chamber. Annealing is known to reduce the rate of spontaneous oxidation of plasma polymers, including those of *trans*-2-butene,[10] a behavior consistent with the somewhat reduced oxygen signatures in the annealed samples. Importantly, the FTIR spectra show no indication of a significant unsaturated (alkene, aromatic, or alkyne)

carbon structure in the 3000-3100 cm^{-1} region. A more detailed discussion of the FTIR spectrum of this plasma polymer can be found elsewhere.[17]

Despite the unconjugated aliphatic nature of the plasma polymer, it has a strong PL response when excited by 405 nm light. The PL emission spectra of the as-deposited and annealed plasma polymers are shown in Figure 2. Normalized by the spectrally-integrated PL signal of the as-deposited plasma polymer, the PL intensity for the as-deposited, 200^0 C annealed, and 300° C annealed plasma polymer are 1.0, 1.4, and 2.1, respectively. The increase in PL cannot be associated with observable change in the unsaturated hydrocarbon content. The emission is centered at 550 nm but the peak is very broad. The PL decays within several nanoseconds but not as a simple exponential as seen in Figure 2; instead, we find that there are an ensemble of decay lifetimes ranging between 10^{-2} and 10^1 ns (not shown). The broad emission and wide lifetime distribution are characteristic of QCPL, which has been observed on the surfaces of inorganic dielectrics and semiconductors and is the result of interactions among a high density of absorbing and luminescing defects.[14] Our PL measurement is confocal and is focused within the bulk of the polymer, not the surface. We do not believe that these defects are based on the sputtering and subsequent incorporation of chamber wall material into the plasma polymer. High atomic number contaminants are detrimental to the performance of HED ablators and extensive x-ray characterization of plasma polymer from this deposition system has not found such contaminants.[18]
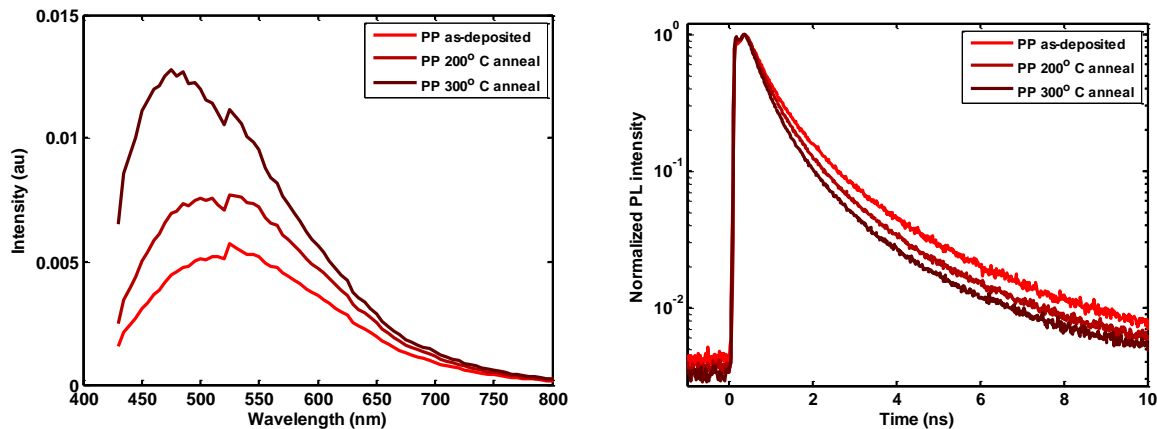
Figure 2. (left) Broad photoluminescence emission spectra for plasma polymer (PP) showing increased signal following annealing. PL signal is normalized to the spectrally-integrated area for the as-deposited PP. (right) Lifetime of PL signal for difference annealing conditions. Note the log scale, demonstrating that the PL does not decay as a simple exponential.

PL in plasma polymers sourced from a variety of conjugated and non-conjugated precursors (e.g., methyl methacrylate,[11] toluene and styrene,[19] thiophene[20]) also display broad PL emission spectra and – in one case[11] – decays similar to those we observe. The ubiquity of this phenomenon may be indicative of a process common to plasma polymerization. Because QCPL has been previously associated with a high density of electronic defects, one possibility is that plasma polymerization in general forms such defects. This would be consistent with the precursor-fragmentation mechanism that occurs during plasma polymerization. We observe that annealing increases the QCPL and therefore it must increase the density of photoactive defects, their absorptivity, or the efficiency with which a defect converts an absorbed photon into an emitted photon (or some combination of the three). While thermal annealing tends to stabilize

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plasma polymers against spontaneous oxidation, the PL spectra suggest that they will become more prone to photo-oxidative degradation. To test this hypothesis, we exposed samples of plasma polymer to blue light (λ=405 nm) from an LED light source under ambient conditions. We chose this wavelength both because it matches the PL excitation wavelength and because the effects of visible light would not be conflated with the well-known phenomenon of UV photo-oxidation of polymers.

Figure 3 shows FTIR spectra in the hydroxyl (left panel) and carbonyl (right panel) regions for the plasma polymer annealed at 300° C at different illumination times. Peaks corresponding to both hydroxyl and carbonyl groups increase in intensity with illumination time. These products are consistent with the classical view of polymer photo-oxidation, where photoexcitation leads to bond-breakage and carbon-centered radicals that can then react with molecular oxygen.[21] Oxidation schemes for hydrocarbon polymers, including plasma polymers, which result in the incorporation of both hydroxyl and carbonyl can be found in the literature.[22] The distinguishing feature of the effect that we observe is that lower photon energies are required to break the bonds in the plasma polymer than in classical polymer photo-oxidation, which typically occurs in the UV region.
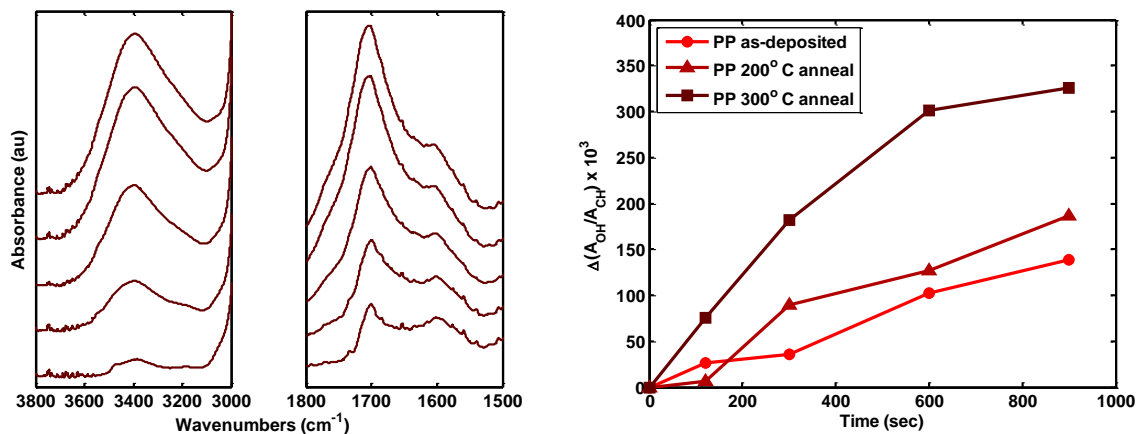
Figure 3. (left) Detail of plasma polymer FTIR spectra showing increased signal in the hydroxyl region (~3400 cm^{-1}) and carbonyl region (~1700 cm^{-1}) following illumination for (bottom to top) 0, 120, 300, 600, and 900 seconds. (right) Increase in integrated OH peak areas (normalized by integrated CH peak area) as a function of illumination time for as deposited and annealed plasma polymer (PP).

Integrating the area under the hydroxyl peak provided a semi-quantitative measure of the extent of oxidation. This area was normalized to the area under the C-H stretching peaks in the 2800-3100 cm^{-1} region. We did not use the area under the carbonyl peak because it is convoluted with the broad array of hydrocarbon stretches in this region, which is typical for plasma polymers. Figure 3 also shows this semi-quantitative measure of oxidation as a function of illumination time for the plasma polymer under three different annealing conditions. The curve for the as-deposited material represents the difference between the oxidation of a sample experiencing illumination and spontaneous oxidation of a witness sample under the same conditions without illumination. This control was not necessary for the thermally annealed samples, since they did not spontaneously oxidize over the experimental time scale. As with the strength of the QCPL, the rate of photo-oxidation increases with annealing temperature. We attempted to saturate the oxidation of the plasma polymer by continued exposure to light, but the material continued to react even after two hours of exposure. Understanding the long-term behavior of the photo-oxidation is an area for future study.

Previous researchers asserted that free radicals in unannealed plasma polymer account for the unusual photosensitivity of plasma polymers.[13] Electron spin resonance spectroscopy of the as-deposited and 300 ^{o}C thermally annealed plasma polymer in this work is shown in Figure 4.

Thermal annealing at 300 °C decreases the free radical content by 40% , consistent with previous reports that thermal annealing quenches the spontaneous oxidation of plasma polymers of *trans*-2-butene.[10] Therefore, the defects responsible for the photo-oxidation are distinct from free radicals formed during the plasma polymerization because thermal annealing increases rather than decreases the photoactivity of these defects.
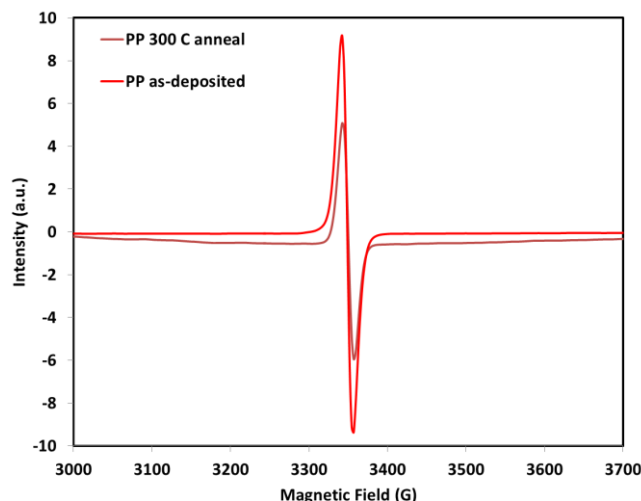

Figure 4. Electron spin resonance spectra of as-deposited and 300 °C annealed plasma polymer (PP). Annealing reduces the free radical concentration by 40%.

Because QCPL is observed even in the as-deposited polymer, the photoactive defects that lead to the photo-oxidation of the plasma polymer are likely formed during the deposition process. This is not altogether surprising considering the complex set of chemical reactions that occur during plasma polymerization, including fragmentation of precursor gases.[2] Different plasma parameters, including duty cycle for pulsed plasma depositions, and precursors gases may affect the photoactivity of the final plasma polymers. However, neither pulsing the plasma nor changing the precursor gas is likely to eliminate these effects entirely. It is known that a pulsed plasma reduces but does not eliminate the defect population.[23] It is also unlikely that the effects

observed here are limited to plasma polymers of *trans*-2-butene. It has been shown that the polymer properties are only weakly dependent on the identity of the hydrocarbon when plasma polymers are grown from a mixture of H_2 and a hydrocarbon, as in this study.[24] Both QCPL[11] (although not noted as such at the time) and unusual photo-oxidation behavior[13] have been observed in plasma polymers of methyl methacrylate. We therefore expect the photoactivity of plasma polymers deposited from different precursors and at different plasma parameters to differ in degree but not kind, although this is an avenue for further study.

The nature of the photoactive defects, which appear to be common to many types of plasma polymer, is as yet unclear. The FTIR spectra in Figure 1 do not show significant alkene contribution, suggesting that the light is not exciting delocalized electrons in conjugated bonds. The appearance of hydroxyl and carbonyl groups following photo-oxidation are not associated with the observable decrease of other FTIR stretches. Identifying the photoactive defects is an important avenue for further research, but is outside the scope of this paper. Still, CVD has many pragmatic advantages as a polymer coating technology,[15, 25] so a CVD polymer that can be synthesized without producing plasma-induced defects may prove to be more stable. We explored this concept by synthesizing films of PDVB using a non-plasma deposition method known as iCVD. This polymer has been previously synthesized by iCVD.[26, 27] iCVD is a vapor phase technique for free-radical polymerization and thin-film deposition of polymers in a single step. The process is carried out in an evacuated chamber with a heated filament (~250-300 °C) providing the energy to generate free radicals from a vapor-phase initiator. The filament temperature is chosen to be lower than the decomposition temperature of the monomer so that – unlike plasma polymerization – monomer fragmentation plays little or no role in the deposition mechanism. The substrate is maintained at lower temperatures (~10-25 °C), promoting

adsorption of the monomer on the substrate surface, where free-radical polymerization and deposition occur.[15, 16]

We chose PDVB as a comparator to the plasma polymer for two reasons. First, and most importantly from the perspective of this study, PDVB is an all-hydrocarbon polymer, making oxidation easy to track by FTIR. Second, PDVB is a highly cross-linked aromatic polymer, which makes it likely to replicate the thermal and mechanical properties of the highly cross-linked hydrocarbon plasma polymer. We did not test these material properties for this study, but solution-synthesized PDVB has been shown to be thermally stable at 300 $^{\circ}$C in inert environments[28, 29] and iCVD-synthesized PDVB has a reported modulus of >5 GPa.[27] Plasma polymer of *trans*-2-butene is stable at 300 $^{\circ}$C in nitrogen[30] and has a modulus of ~3 GPa. The properties of hydrocarbon plasma polymers are relatively insensitive to the identity of the hydrocarbon precursor, thereby facilitating a comparison between CVD processes despite the use of different precursors. [24] To confirm this behavior, we deposited plasma polymer using DVB as the precursor. The FTIR, PL and UV-Vis spectra do not differ significantly between the plasma polymers deposited using DVB or *trans*-2-butene as the precursor (data not shown).

The as-deposited FTIR spectrum of iCVD PDVB in Figure 5 is in good agreement with previous iCVD results as determined by Petruczok *et al*.[27] The lack of plasma-induced fragmentation in the iCVD process results in an FTIR spectrum with much narrower peak widths than the plasma polymer. Instead, the peaks in the PDVB spectrum can be assigned to functional groups consistent with the structure of the aromatic DVB monomer. This is evident in the three stretches at 3019 cm^{-1}, 3047 cm^{-1}, and 3084 cm^{-1} corresponding to aromatic C-H stretching of ring hydrogens.[31] Also retained in the iCVD PDVB samples are C-C absorptions in the 1400-1600 cm^{-1} region characteristic of 1,3 and 1,4 substituted aromatic rings,[31] which should be

expected from the mixture of *m*-DVB and *p*-DVB used as the monomer. These peaks provide strong evidence that the aromatic structure is retained in the as-deposited polymer. In addition, there is a small indication of OH bonding in the 3400-3500 cm^{-1} region in the as-deposited polymer. This feature disappears after annealing, likely due to desorption or removal of a small amount of adventitious water in the polymer.
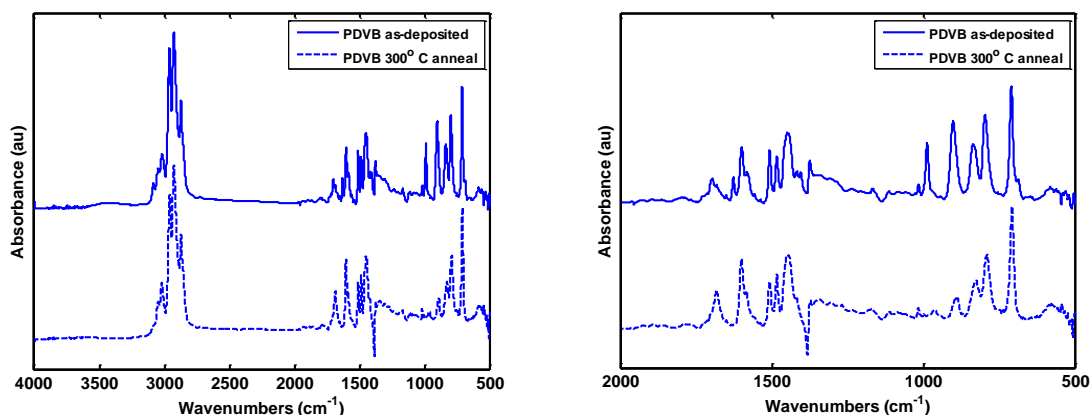

Figure 5. (left) FTIR spectra for as-deposited and annealed PDVB and (right) detail of the fingerprint region.

   Not all of the pendant vinyl groups on DVB were consumed during the polymerization, most likely due to steric effects. This is clear from the vinyl stretches that are still present in the as-deposited film at 903 cm^{-1}, which corresponds to CH_2 out-of-plane bending on vinyl groups, as well as at ~990 cm^{-1} and ~1630 cm^{-1}, corresponding to C-H deformation in vinyl groups and C=C stretching, respectively.[31] An analysis by Petruczok *et al.* showed that approximately half of the incorporated DVB monomers in iCVD-synthesized PDVB had one unreacted pendant vinyl group.

The characteristic peaks corresponding to unreacted pendant vinyl at 903 cm^{-1}, 990 cm^{-1}, and 1630 cm^{-1} are all significantly reduced in the post-anneal spectrum. The reaction of pendant vinyl groups is consistent with previous work on solution-synthesized PDVB, where residual pendant groups underwent thermal coupling reactions during annealing in an inert atmosphere.[29] These observations match well with the results presented here, in that we see a reduction, but not total elimination, of the pendant vinyl after annealing, as well as some small shifts or rearrangements in the C-C and C-H region. In our case, annealing was performed under an inert atmosphere and we do not see evidence of oxidation in the spectra of the annealed samples. The thermal stability of the PDVB upon annealing suggests that they are reasonably highly cross-linked.

A striking difference between the PDVB and the plasma polymer can be observed in the photograph in Figure 6: the plasma polymer has a yellowish tinge and PDVB is visually clear. The slight yellow color is a hallmark of plasma polymers and has been observed previously.[11, 32] The ultraviolet-visible (UV-Vis) transmission spectra in Figure 6 also show this difference: PDVB has a sharp absorption edge between 290-310 nm whereas the plasma polymer has a broad edge between 200 -500 nm. Based on this absorption behavior it is perhaps unsurprising that the plasma polymer shows photoactivity at 405 nm. The PDVB is essentially transparent in the visible wavelengths; the undulations in Figure 6 are due to interference through the transparent film.
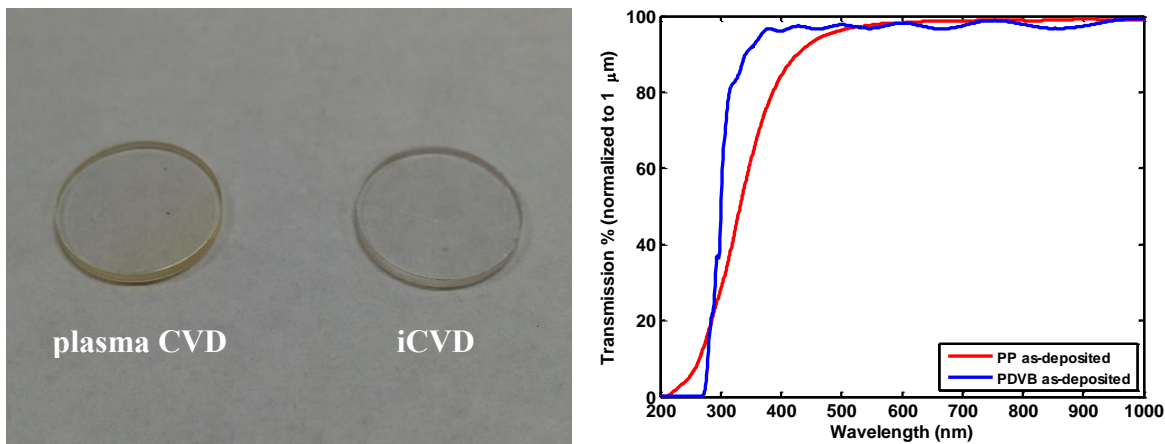
Figure 6. (left) Photograph of plasma polymer and iCVD PDVB ~1 μm films on 13 mm diameter discs. (right) UV-Vis transmission curves for as-deposited plasma polymer (PP) and PDVB, normalized to 1 μm film thickness.

The relative transparency of PDVB at 405 nm is accompanied by a PL signal that is 1000× weaker than that of the plasma polymer, as shown in Figure 7. The spectrally-integrated PL signal for the as-deposited PDVB (normalized as before by the spectrally-integrated signal PL signal for the as-deposited plasma polymer) is only 6.3×10^{-4}. The chemical pathways during plasma polymerization rely upon fragmentation of the precursor gas and so the unusually strong PL in the plasma polymer may be indicative of defects formed during the plasma-induced fragmentation. By contrast, the polymerization pathways in iCVD are essentially those of traditional free-radical polymerization and the dramatically lower level of PL in the PDVB suggests that the lack of such fragmentation leads to fewer photoactive defects.
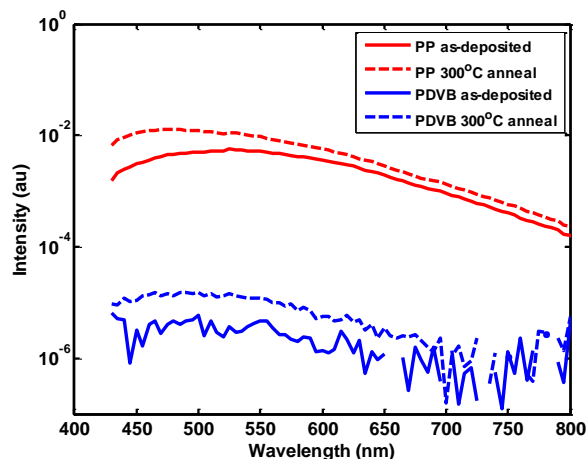
Figure 7. Photoluminescence emission spectra for as-deposited and annealed plasma polymer (PP) and PDVB. Intensity is normalized to the spectrally-integrated PL signal for the as-deposited PP. The log scale facilitates comparison across decades. Data for PP are the same as those shown in Figure 2.

Consistent with its much lower PL, the iCVD PDVB is more stable to photo-oxidation under blue light than the plasma polymer. FTIR traces of PDVB after various illumination times are shown in Figure 8; there is no observable change. The OH peak area in the PDVB as a function of illumination time is also shown in Figure 8. Shown for comparison is the plasma polymer photo-oxidation from Figure 3. Within our ability to quantify oxidation, the PDVB is stable to photo-oxidation relative to the plasma polymer. Annealing makes PDVB slightly more susceptible to photo-oxidation under blue light illumination, again consistent with the PL data. Still, the annealed PDVB is more resistant to photo-oxidation than any of the plasma polymers tested.
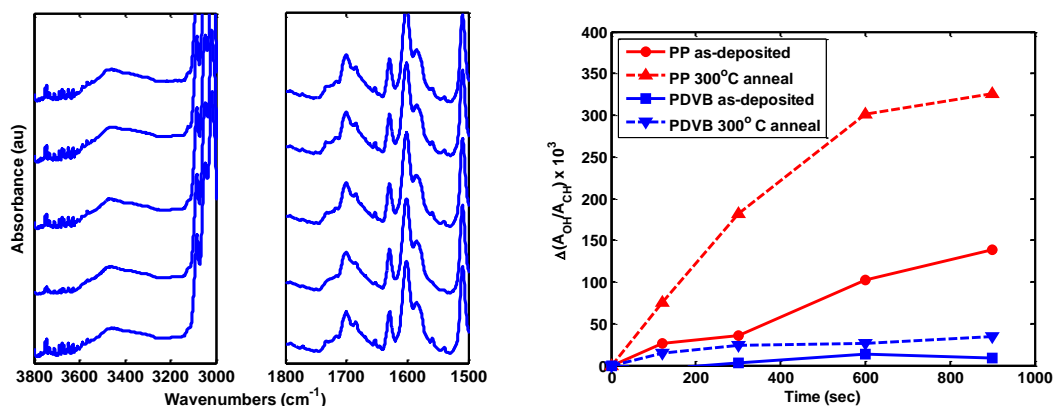
Figure 8. (left) PDVB FTIR spectra detailing hydroxyl region (left panel) and carbonyl region (right panel) following illumination for (bottom to top) 0, 120, 300, 600, and 900 seconds. (right) Increase in integrated OH peak areas (normalized by integrated CH peak area) as a function of illumination time for as deposited and annealed plasma polymer (PP) and PDVB. Data for PP are the same as those shown in Figure 3.

Conclusions

CVD polymers offer several advantages over liquid coating strategies, such as single-step casting and synthesis, solvent-free operation, and conformal coating. However, the lack of chemical stability of plasma polymers has been one of the major barriers to their adoption. The unusual PL behavior of plasma polymers has long been noted and in this work we have shown that the photostability of plasma polymers of *trans*-2-butene is linked to its PL behavior. The PL is consistent with QCPL seen on inorganic surfaces and is likely the result of photoactive defects formed during the plasma polymerization. By using blue light to excite these defects for both PL and photo-oxidation experiments, we have shown that the reaction with molecular oxygen under illumination is distinct from classical UV-induced degradation of polymers. The connection between photo-oxidation and QCPL suggests that PL measurements may be used as a diagnostic for the photostability of polymeric and other materials.

The results presented here show that photo-oxidation results in the formation of carbonyl and hydroxyl moieties in the plasma polymer. Known UV photo-oxidative pathways form both of these products, although the use of lower energy blue light distinguishes the results presented in this work. Photo-oxidation by these lower energy photons is not observed in traditional polymers, and free radicals in the plasma polymer cannot account for this observation. We quenched the activity of the free radicals contained in the plasma polymer via annealing and found that the photostability decreased, rather than increased. One area of further investigation is to understand why this is so. If the photo-oxidation eventually saturates, then it may be possible to tell whether annealing actually increases the density of reactive sites or whether it simply changes the rate at which they react. The dose-response behavior of these materials is also an area for future study, as it is currently unknown whether the extent of photo-oxidation is driven by total accumulated dose or intensity.

Nevertheless, removing monomer fragmentation from the polymerization pathway suggests a pathway for synthesizing chemically stable CVD polymers. A non-plasma method such as iCVD is a good candidate because the film properties are not dependent on processes that damage the monomer. Other non-plasma CVD methods such as parylene deposition[33] or molecular layer deposition[34] may also provide photostability. These non-plasma methods may therefore offer a route to photochemically robust hydrocarbon CVD polymers, enabling adoption in applications where long-term exposure to engineering use conditions is critical.

Experimental

Plasma polymer film fabrication. Plasma polymers of *trans*-2-butene were synthesized in a custom-built inductively-coupled plasma chamber as previously described. [5, 30] *Trans*-2-butene

(95%, Matheson Tri-Gas) and hydrogen (Ultra-high purity grade, Air Liquide) flowed into the chamber at flowrates of ~0.1 sccm and 10 sccm, respectively, with the chamber pressure maintained at 100 mTorr. The plasma frequency was 43015 kHz and the power was 13.5 W, resulting in a deposition rate of approximately 8-10 nm/min. Plasma polymer was deposited on potassium bromide (KBr) substrates (for infrared characterization) or fused quartz (for UV-Vis characterization). Following deposition, some samples were annealed for 26 hours in a tube furnace under flowing nitrogen at either 200 $^{\circ}$C or 300 $^{\circ}$C. Annealed samples were stored under flowing nitrogen until use, while unannealed samples were stored in the deposition chamber at reduced pressure (~1 mTorr). Samples were coated for 100 minutes to a thickness of approximately 1 μm.

iCVD film fabrication. Deposition of PDVB by iCVD was carried out in a custom-designed pancake-shaped reactor approximately 250 mm in diameter and 50 mm deep (GVD Corporation) equipped with an array of resistively heated nichrome filaments (Omega NI80-020) suspended above the deposition stage. DVB monomer (Sigma Aldrich, technical grade, 80%) was heated to 70° C in a jar and the vapor fed to the chamber (3.0 sccm) through a heated (75-80 $^{\circ}$C) needle valve and delivery line. A small amount of $CuCl_2$ as was added to the monomer to inhibit thermal auto-polymerization inside the jar. The initiator *tert*-butyl peroxide (TBPO, Sigma Aldrich, 98%) was fed to the chamber (~0.2 sccm) as a vapor from a separate jar and delivery line. Reagents were used as-received and without further purification. DVB and TBPO vapors flowed into the reactor that was maintained at 150 mTorr. The filament array in the reactor was maintained at 300° C using a variable transformer and a thermocouple attached to a section of the array. The sample stage was water-cooled to 12° C using a recirculating chiller (Thermo Scientific Neslab RTE 7). PDVB films approximately 1 μm in thickness were deposited on KBr

substrates (for infrared characterization) or fused quartz (for UV-Vis characterization). A silicon wafer was used during each run to monitor the progress of the deposition via laser interferometry using a procedure described previously.[35]

Polymer characterization. Samples were characterized by FTIR spectroscopy (Thermo-Fisher, Nicolet iS10) and peak areas were integrated using vendor-supplied software (OMNIC and Macros Basic). An uncoated KBr disc was used as a background sample and all spectra are averages of at least 32 scans at .482 cm^{-1} resolution. UV-Vis transmission spectra (Ocean Optics USB2000+XR1 spectrometer with DH-2000-BAL deuterium/halogen light source) were measured on samples deposited on fused quartz slides. The transmission spectra were integrated for 1 ms and averaged over 1000 scans. An uncoated fused quartz slide was used as a background and Beer's Law was used to normalize the transmission to a 1 micron equivalent thickness.

PL measurements were made on a home-built setup described in detail elsewhere.[14, 36] Briefly, a 405 nm wavelength pulsed laser (150 ps) was focused on the sample using a 50×, 0.95 NA objective (Zeiss). PL excited by the laser was collected through the same objective, transmitted through a dichroic mirror (430 DRLP, Omega Optical), and focused onto a 150 μm confocal pinhole. A narrow spectral band of the collected PL was selected using a monochromator/spectrometer (Acton 300i), and focused onto an avalanche photodiode (PDM 50CT, Micro Photon Devices). The PL lifetime was measured by recording the arrival time of each detected photon relative to the laser pulse using a time-to-digital converter (PicoHarp 300, Picoquant).

ESR measurements (Bruker, ELEXSYS E500) were obtained on plasma polymer scraped off of a silicon deposition substrate. The annealed sample was annealed following removal from the

substrate. The spectrometer operated under the X band with a power level of 0.6 mW. The modulation frequency was 100 kHz with an amplitude of 2 G and a conversion time of 100ms. Sweep times were sufficiently slow as to not allow for dispersions in the resonances and there was no observed saturation. Each sample was weighed to 10 mg +/- 0.05 mg and placed in the same part of the resonant cavity; the cavity was tuned such that the Q matched for each sample.

Photo-oxidation experiments. A blue light emitting diode (Bluepoint, Honle UV America, output wavelength centered at 405 nm) was used for photo-oxidation experiments. Samples on 13 mm KBr discs were placed 25 mm away from the light source (~500 mW/cm^2) and illuminated under ambient conditions (~50% RH, 21% oxygen).

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TOC Graphic
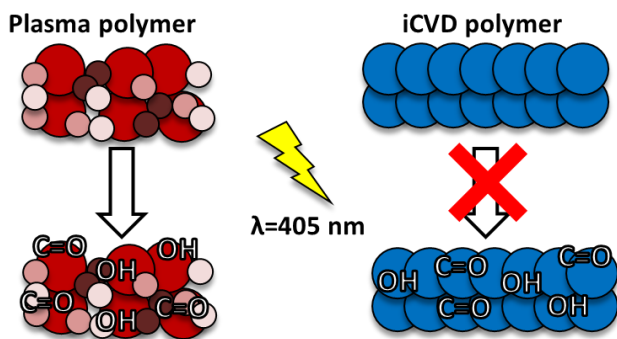
TOC Text

The photo-oxidative stability of hydrocarbon polymers deposited via plasma and initiated chemical vapor deposition (iCVD) is compared. The plasma polymer has an unusually strong and broad photoluminescence emission when excited with blue light. The strength of the photoluminescence is correlated with its rate of photo-oxidation under blue light illumination. The iCVD polymer has 1000× weaker photoluminescence signal and is far more photo-stable.